

XANES Study of Ru Valence in Magnetoresistive Ru-based Perovskites

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Introduction: Doping of Ru-based perovskite compounds by LaFeO_3 or LaCoO_3 leads to materials, which possess a large magnetoresistance at low temperatures. The knowledge of the valence state of Ru ions in those compounds is essential for understanding of the observed MR effect. For that purpose, x-ray absorption near-edge spectroscopy (XANES) is a unique tool, which provides nondestructive method of studying of valence state of selected ions in the material.

Methods and Materials: Ru L_{III} -edge XANES spectra in a series of compounds: $\text{Sr}_{1-x}\text{La}_x\text{Ru}_{1-x}\text{Fe}_x\text{O}_3$, $\text{Ca}_{1-x}\text{La}_x\text{Ru}_{1-x}\text{Fe}_x\text{O}_3$, $\text{Sr}_{1-x}\text{La}_x\text{Ru}_{1-x}\text{Co}_x\text{O}_3$ and $\text{SrRu}_{1-x}\text{Co}_x\text{O}_3$, have been investigated. The spectra were collected at room temperature and analyzed with respect to the reference materials SrRuO_3 , CaRuO_3 , RuO_2 and $\text{SrY}_{1/2}\text{Ru}_{1/2}\text{O}_3$, in which Ru is either tetravalent or pentavalent.

Results: Valence state of Ru in the parent perovskites SrRuO_3 or CaRuO_3 is Ru^{4+} . Upon doping by Fe-containing compounds, Ru preserves its tetravalent state (Fig. 1). On the other hand, doping by Co induces charge transfer from Ru to Co, thus leaving Ru pentavalent. This process as a function of dopant concentration, represented by gradual shift of absorption peaks toward higher energies due to the increasing amount of Ru^{5+} in compound, is shown on Fig. 2.

Such findings regarding the charge state of Ru are in a complete agreement with magnetic properties observed in these compounds.

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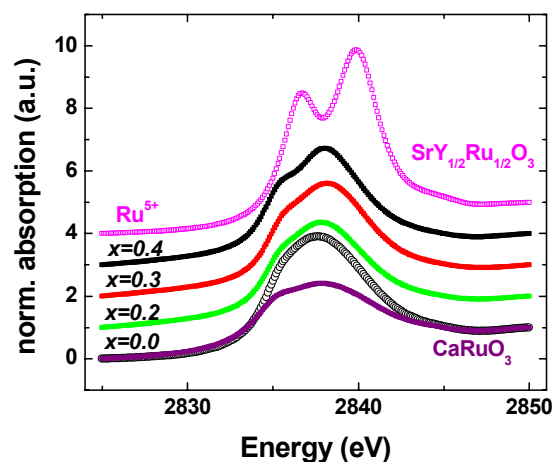


Fig. 1. Ru L_{III} -edge XANES spectra of $\text{Sr}_{1-x}\text{La}_x\text{Ru}_{1-x}\text{Fe}_x\text{O}_3$ compounds indicating presence of tetravalent Ru ion. For reference spectra of CaRuO_3 and $\text{SrY}_{1/2}\text{Ru}_{1/2}\text{O}_3$ are shown.

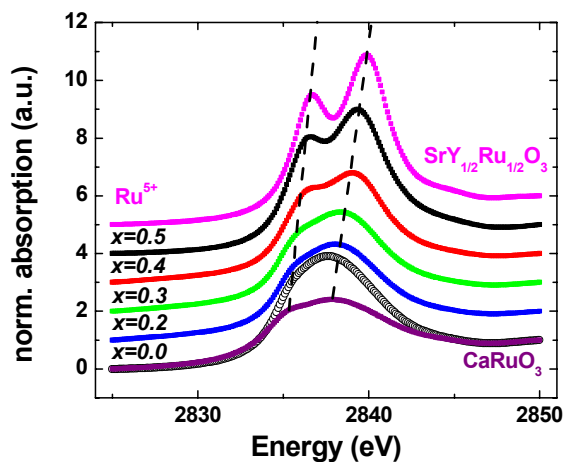


Fig. 2. Ru L_{III} -edge XANES spectra of $\text{Sr}_{1-x}\text{La}_x\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ compounds. For reference spectra of CaRuO_3 and $\text{SrY}_{1/2}\text{Ru}_{1/2}\text{O}_3$ are shown. Dashed lines show shift of peaks positions toward higher energies, indicating increase in concentration of Ru^{5+} ion.